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(54) Title: LOW COLOR PROCESSING, HEAT AND LIGHT STABILIZER SYSTEM FOR POLYPROPYLENE FIBER			
(57) Abstract Blends of long chain N,N-dialkylhydroxylamines, selected phosphites and selected hindered amines are surprisingly effective in providing processing, long term heat aging and light stability performance and especially gas fade resistance to polypropylene fibers in the absence of a traditionally used phenolic antioxidant.			

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Low Color Processing, Heat and Light Stabilizer System for Polypropylene Fiber

The instant invention pertains to stabilized polypropylene fiber, free or essentially free of any traditionally used phenolic antioxidant, and having enhanced light stability, enhanced long term heat stability and especially enhanced gas fade resistance. This fiber formulation is stabilized by an effective amount of a mixture of a selected hindered amine, a selected hydroxylamine and a selected phosphite.

Polypropylene fiber is traditionally stabilized with a blend of selected phenolic antioxidant, selected phosphite and selected hindered amine light stabilizer. This formulation generally provides adequate processing, heat and light stabilization performance, but does not provide adequate gas fade resistance which is needed to maintain color properties during storage and end-use application. There is a long-felt need in the marketplace for a stabilizer system which can prevent this gas fading and color formation associated with the use of phenolic antioxidants. Gas fading is known in the industry as a discoloration resulting from the exposure of plastic articles to an atmosphere containing oxides of nitrogen.

The components of the instant stabilizer system for polypropylene fibers are generically well-known as stabilizers for a host of organic and polymeric substrates. The components of the instant stabilizer system for polypropylene fiber are a specific combination of selected 2,2,6,6-tetramethylpiperidine hindered amines, phosphites or phosphonites and N,N-dialkylhydroxylamines, in the absence or essential absence of a phenolic antioxidant. This instant stabilizer formulation provides unexpectedly superior gas fade resistance, and heat and light stability performance properties to the polypropylene fibers which are notoriously difficult to stabilize effectively. The instant phenolic free antioxidant stabilizer system provides the best overall stabilization for polypropylene fiber. Discoloration of polypropylene fibers, when exposed to an atmosphere containing oxides of nitrogen, i.e. gas fading conditions, encountered with stabilizer systems containing phenolic antioxidants, makes such systems unacceptable in this important property even though in other performance criteria the phenolic antioxidants perform adequately.

- 2 -

The hindered amines are a very important class of light and thermal stabilizers based on compounds having a 2,2,6,6-tetramethylpiperidine moiety somewhere in the molecule. These compounds have achieved great commercial success and are well-known in the art.

Likewise, phosphonites or phosphites such as those described in US-A-4 360 617 have also achieved great commercial success as stabilizers.

N,N-Dialkylhydroxylamines also are known in the art as seen in US-A-4 590 231, US-A-4 782 105, US-A-4 876 300 and US-A-5 013 510. These compounds are useful as process stabilizers for polyolefins when used alone or in combination with phenolic antioxidants and/or other coadditives, particularly as taught in US-A-4 876 300. Although US-A-4 876 300 teaches generically that N,N-dialkylhydroxylamines can be used in combination with phenolic antioxidants, hindered amines, phosphites, UV absorbers and other additives, there is no specific disclosure that polypropylene fibers can be beneficially stabilized by specific combinations of selected hindered amines, phosphites or phosphonites and N,N-dialkylhydroxylamines. Thus the instant invention is essentially a selection from within the broad generic scope of US-A-4 876 300.

However, the instant composition is distinguished from the compositions of the prior art in several important aspects listed below:

1. Hindered phenolic antioxidants plus phosphites combinations have generally poor gas fade resistance;
2. Phosphites alone lack adequate process and thermal stabilization efficacy; and
3. Phosphites plus hindered amines lack adequate process stabilization.

The instant combination of stabilizers provide all of the required requisites of gas fade resistance and process and thermal stability.

The object of this invention is to provide a stabilizer system for polypropylene fiber, in the absence of any traditionally used phenolic antioxidant or in the presence of only very low levels of phenolic antioxidant, which would allow the polypropylene fibers to have enhanced light and long term heat stability and especially enhanced gas fade resistance while maintaining process stabilization comparable to any system using phenolic antioxidants.

Another object of the instant invention is to provide a method to improve gas fade re-

- 3 -

sistance and to reduce color formation in polypropylene fibers by using the instant stabilizer system free of phenolic antioxidant.

The instant invention pertains to stabilized polypropylene fiber, free or essentially free of any phenolic antioxidant, and having enhanced light stability, enhanced long term heat stability and enhanced gas fade resistance, which fiber is stabilized by a mixture of

a) a hindered amine selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;

the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;

N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;

poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;

bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethylmalonate;

1,3,5-tris{N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-s-triazine};

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-cyclohexylamino-s-triazine; and

poly{N-[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,4,7-triazanonane}- ω -N''-[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]amine;

b) a phosphite selected from the group consisting of

tris(2,4-di-tert-butylphenyl) phosphite;

3,9-di(2,4-di-tert-butylphenyl)-2,4,8,10-tetraoxa-3,9-diphospha[5.5]undecane;

2,2',2''-nitrilo-tris[ethyl (3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite];

ethyl bis(2,4-di-tert-butyl-6-methylphenyl) phosphite; and

tetrakis(2,4-di-tert-butylphenyl)-4,4'-bis(diphenylene)phosphonite; and

c) a hydroxylamine selected from the group consisting of

- 4 -

N,N-dioctadecylhydroxylamine;

N,N-dialkylhydroxylamine of the formula T_1T_2NOH where T_1 and T_2 are the alkyl mixture found in hydrogenated tallow amine; and

the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901;

wherein the weight ratio of components (a):(b):(c) is from 1:1:1 to 100:2:1; preferably 10:1:1 to 10:2:1; and most preferably 6:1:1 to 6:2:1.

The effective amount of the mixture of stabilizers is from 0.05 to 5 %, preferably 0.1 to 2 %, most preferably 0.15 to 1 %, by weight based on the weight of the fiber.

Stabilized polypropylene fiber which are of particular interest are those where the component (a) is selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;

the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;

N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;

poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;

bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethylmalonate; and

1,3,5-tris{N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-s-triazine.

Stabilized polypropylene fiber which are also of particular interest are those where the component (b) is selected from the group consisting of

tris(2,4-di-tert-butylphenyl) phosphite;

3,9-di(2,4-di-tert-butylphenyl)-2,4,8,10-tetraoxa-3,9-diphospha[5.5]undecane;

2,2',2''-nitrido-tris[ethyl (3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite];

and

- 5 -

ethyl bis(2,4-di-tert-butyl-6-methylphenyl) phosphite.

Stabilized polypropylene fiber which are particularly preferred are those where the component (c) is the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901.

Additionally, the instant invention also pertains to a binary stabilizer system where the stabilized polypropylene fiber, free or essentially free of any phenolic antioxidant, and having enhanced light stability, enhanced long term heat stability and enhanced gas fade resistance, which fiber is stabilized by a mixture of

I) a hindered amine selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;

the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;

N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;

poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;

bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethylmalonate;

1,3,5-tris{N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-s-triazine; and

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-cyclohexylamino-s-triazine; and

II) a hydroxylamine selected from the group consisting of

N,N-dioctadecylhydroxylamine;

N,N-dialkylhydroxylamine of the formula T_1T_2NOH where T_1 and T_2 are the alkyl mixture found in hydrogenated tallow amine; and

the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901;

- 6 -

wherein the weight ratio of components (I):(II) is from 100:1 to 1:2; preferably 10:1 to 1:1; and most preferably 5:1 to 3:1.

Binary stabilized polypropylene fiber which are of particular interest are those where the component (I) is selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;
the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid; and
N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane.

Binary stabilized polypropylene fiber which are of particular interest are those where the component (II) is the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901.

The effective amount of the mixture of stabilizers is from 0.05 to 5 %, preferably 0.1 to 2 %, most preferably 0.15 to 1 %, by weight based on the weight of the fiber.

The instant invention involves a selected mixture of stabilizers which are free or essentially free of any phenolic antioxidants. Some manufacturers of polypropylene add tiny amounts, usually <0.01 % by weight of phenolic antioxidant, to aid in the initial manufacture of the polypropylene resin. The amount of phenolic antioxidant remaining in the resin used to prepare polypropylene fiber is far less than the 0.05% by weight of phenolic antioxidant used in the working examples of US-A-4 876 300. As the phrase free or essentially free of phenolic antioxidant as used in the context of the instant invention means 0 to 0.01 % by weight of phenolic antioxidant may be present in the instant compositions. No phenolic antioxidant is deliberately added to the instant compositions in order to achieve the stabilization efficacies described.

Another most important aspect of the instant invention is to a method for improving gas fade resistance and reducing color formation in stabilized polypropylene fiber by incorporating therein an effective stabilizing amount of the mixture of stabilizers described above with out the loss of any other stabilization property.

Still another aspect of the instant invention is to a method for enhancing the resistance to

- 7 -

degradation of polypropylene fiber, due to exposure to UV radiation over that which can be achieved by the use of conventional stabilizers alone, by incorporating therein an effective stabilizing amount of the mixture of stabilizers described above.

Yet another aspect of the instant invention is to a method for enhancing the thermal stability of polypropylene fiber, over that which can be achieved by the use of conventional stabilizers alone, by incorporating therein an effective stabilizing amount of the mixture of stabilizers described above.

The cited hindered amines and phosphites are generally commercially available or can be made by published methods.

The N,N-dialkylhydroxylamines are prepared by methods disclosed in US-A-4 782 105; US-A-4 898 901 and particularly US-A-5 013 510 by the direct oxidation of N,N-di-(hydrogenated tallow)amine by hydrogen peroxide.

The polypropylene fiber may also contain other additives such as fillers and reinforcing agents such as calcium carbonate, silicates, glass fibers, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite and other additives, for example, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame-proofing agents and anti-static agents.

Conventional stabilization systems, such as phenolic antioxidant with phosphite and hindered amine stabilizer, or phosphite with hindered amine stabilizer, can provide excellent stabilization to polypropylene fibers in selected performance areas, but it is only through the use of the instant ternary combination of a selected hindered amine, selected hydroxylamine and selected phosphite that all important performance properties for stabilized polypropylene fibers can be optimized.

Polypropylene is used extensively for the manufacture of fiber for residential, commercial and automotive carpeting. White and light-colored fiber can suffer from discoloration due to gas fade discoloration. Polypropylene resin as it is originally manufactured may contain very low levels of phenolic antioxidant for stability till said resin is later fabricated into fiber. In each case some additional stabilizer package must be added to the propylene resin before fabrication into fiber is possible. Hindered phenolic antioxidants are well-known as a potential source of such discoloration by the formation of quinone type chromophores as

- 8 -

oxidation products or as the result of environmental exposure to the oxides of nitrogen (known as "gas fade" discoloration).

It is therefore desirable to remove the phenolic antioxidant component from the polypropylene fiber. Unfortunately when this has been done in the past, other properties related to polymer stability are adversely effected. Phenolic antioxidants protect the polymer during high temperature melt processing, extrusion and spinning operations. Phenolic antioxidants further protect the polymer pellets and resultant fiber during storage and final end-use applications.

Surprisingly, it was found that the phenolic antioxidant could be replaced in the instant stabilizer system which is a ternary combination of a selected hindered amine, a selected hydroxylamine and a selected phosphite or a binary combination of a selected hindered amine and a selected hydroxylamine. Said system provides stability in excess of that obtained with conventional stabilizer systems having a phenolic antioxidant component without the discoloration associated with the phenolic antioxidant when the stabilized polypropylene fiber is exposed to gas fading conditions, i.e. in an atmosphere containing the oxides of nitrogen.

The following examples are presented for the purpose of illustration only and are not to be construed to limit the nature or scope of the instant invention in any manner whatsoever.

Test Compounds:

- AO A = 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate;
- HALS 1 = the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;
- HALS 2 = the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;
- HALS 3 = N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)-amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;
- HALS 4 = the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-

- 9 -

tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;

- HALS 5 = poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;
- HALS 6 = bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethyl-malonate;
- HALS 7 = 1,3,5-tris{N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)-ethyl]amino-s-triazine};
- Phos I = tris(2,4-di-tert-butylphenyl) phosphite;
- Phos II = 3,9-di(2,4-di-tert-butylphenyl)-2,4,8,10-tetraoxa-3,9-diphospha[5.5]undecane;
- Phos III = 2,2',2"-nitrido[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite];
- Phos IV = ethyl bis(2,4-di-tert-butyl-6-methylphenyl) phosphite; and
- HA A = the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901.

All additives are designated in % by weight based on the polypropylene. All formulations also contain 0.05% by weight of calcium stearate.

Example 1: Process Stabilization of Polypropylene Fiber.

Fiber grade polypropylene, containing 0.05 % by weight of calcium stearate, is dry blended with the test additives and then melt compounded at 246°C into pellets. The pelletized fully formulated resin is then spun at 274°C into fiber using a Hills laboratory model fiber extruder. The spun tow of 41 filaments is stretched at a ratio of 1: 3.2 to give a final denier of 615/41.

The melt flow rates of the formulated pellets before spinning and of the spun fiber tow

- 10 -

after spinning are determined by ASTM 1238-86. The closer are the melt flow rates before and after spinning, the more effective is the process stabilization efficacy of the stabilizer system. The processing stability data are given in Tables 1, 2, 3 and 4 below.

Table 1:

Stabilizer	Amount	Melt Flow Rate	
		Pellets	Fiber
HALS 1 Phos I HA A	0.30 % 0.09 % 0.01 %	15.4	20.7
HALS 1 Phos I HA A	0.30 % 0.05 % 0.05 %	14.9	19.6
HALS 1 Phos I HA A	0.05 % 0.09 % 0.01 %	13.6	17.7
HALS 1 Phos I HA A	0.05 % 0.05 % 0.05 %	13.6	18.8
AO A HALS 1 Phos I HA A	0.05 % 0.05 % 0.05 % 0.05 %	14.3	19.3

- 11 -

Table 2:

Stabilizer	Amount	Melt Flow Rate	
		Pellets	Fiber
HALS 2 Phos I HA A	0.30 % 0.09 % 0.01 %	13.7	18.6
HALS 2 Phos I HA A	0.30 % 0.05 % 0.05 %	13.8	18.3
HALS 2 Phos I HA A	0.05 % 0.09 % 0.01 %	13.4	17.8
HALS 2 Phos I HA A	0.05 % 0.05 % 0.05 %	14.4	18.7
AO A HALS 2 Phos I HA A	0.05 % 0.05 % 0.05 % 0.05 %	12.9	18.1

Table 3:

Stabilizer	Amount	Melt Flow Rate	
		Pellets	Fiber
HALS 3 Phos I HA A	0.30 % 0.09 % 0.01 %	13.3	19.3
HALS 3 Phos I HA A	0.30 % 0.05 % 0.05 %	14.2	17.5
HALS 3 Phos I HA A	0.05 % 0.09 % 0.01 %	14.3	18.6
HALS 3 Phos I HA A	0.05 % 0.05 % 0.05 %	13.7	18.4
AO A HALS 3 Phos I HA A	0.05 % 0.05 % 0.05 % 0.05 %	12.8	17.5

- 12 -

Table 4:

Stabilizer	Amount	Melt Flow Rate	
		Pellets	Fiber
HALS 2 Phos II HA A	0.05 % 0.05 % 0.05 %	12.7	16.9
AO A HALS 2 Phos II HA A	0.05 % 0.05 % 0.05 % 0.05 %	12.9	16.2

Inspection of the data given above shows that the instant formulations containing selected hindered amines, phosphites and hydroxylamines provide excellent process stabilization to polypropylene fully comparable to stabilizer systems containing phenolic antioxidants.

Example 2: Process Stabilization of Polypropylene Fiber

Melt flow differences resulting from insufficient processing stability can be even more evident when the polypropylene is spun under more severe processing conditions. In Example 1 the polypropylene is spun at 274°C. However, it is not unusual for polypropylene to be spun at much higher temperature at 302°C. The melt flow values of polypropylene spun at such temperatures are shown in the Tables 5, 6, 7 or 8 below.

- 13 -

Table 5:

Stabilizer	Amount	Melt Flow Rate	
		Fiber Spun at 274°C	Fiber Spun at 302°C
Phos I	0.15 %	14.6	26.9
Phos I AO A	0.10 % 0.05 %	13.3	15.5
Phos I AO A	0.05 % 0.05 %	12.7	16.1
Phos I HA A	0.10 % 0.05 %	13.5	16.2
HALS 2 Phos I	0.05 % 0.10 %	15.7	31.9
HALS 2 Phos I AO A	0.05 % 0.10 % 0.05 %	14.3	16.3
HALS 2 Phos I HA A	0.05 % 0.05 % 0.05 %	13.7	17.4
HALS 2 Phos I HA A	0.05 % 0.10 % 0.05 %	13.6	16.1

- 14 -

Table 6:

Stabilizer	Amount	Melt Flow Rate	
		Fiber Spun at 274°C	Fiber Spun at 302°C
Phos II	0.15 %	13.7	20.1
Phos II AO A	0.10 % 0.05 %	13.0	16.5
HALS 2 Phos II	0.05 % 0.10 %	15.2	22.2
HALS 2 Phos II AO A	0.05 % 0.10 % 0.05 %	12.2	15.5
HALS 2 Phos II HA A	0.05 % 0.05 % 0.05 %	12.4	15.5
HALS 2 Phos II HA A	0.05 % 0.10 % 0.05 %	12.7	15.6

- 15 -

Table 7:

Stabilizer	Amount	Melt Flow Rate	
		Fiber Spun at 274°C	Fiber Spun at 302°C
Phos I	0.15 %	14.6	26.9
Phos I AO A	0.10 % 0.05 %	13.3	15.5
HALS 3 Phos I	0.05 % 0.10 %	14.8	31.4
HALS 3 Phos I AO A	0.05 % 0.10 % 0.05 %	13.5	15.1
HALS 3 Phos I HA A	0.05 % 0.05 % 0.05 %	12.4	16.9
HALS 3 Phos I HA A	0.05 % 0.10 % 0.05 %	12.9	16.7

- 16 -

Table 8:

Stabilizer	Amount	Melt Flow Rate	
		Fiber Spun at 274°C	Fiber Spun at 302°C
Phos II	0.15 %	13.7	20.1
Phos II AO A	0.10 % 0.05 %	13.0	16.5
HALS 3 Phos II	0.05 % 0.10 %	14.1	22.8
HALS 3 Phos II HA A	0.05 % 0.05 % 0.05 %	13.1	14.9
HALS 3 Phos II HA A	0.05 % 0.10 % 0.05 %	12.5	15.4

The data in Tables 5, 6, 7 and 8 clearly show that in a conventional stabilizer system a combination of phenolic antioxidant and phosphite provide good processing stability. The removal of the phenolic antioxidant in the presence or absence of a hindered amine results in a significant loss in process stabilization. However, the substitution of a hydroxylamine in place of the phenolic antioxidant yields process stabilization fully comparable to that provided by the phenolic antioxidant-phosphite system.

As is seen in Example 5, however, the presence of phenolic antioxidant in stabilizer systems has a detrimental effect on gas fade resistance.

Example 3: Light Stabilization of Polypropylene Fiber.

The fibers are also exposed to UV light and to long term thermal aging under standard conditions.

Socks knitted from the stabilized polypropylene fibers are exposed in an Atlas Xenon-Arc-WeatherOmeter using the SAE J1885 Interior Automotive conditions at 89°C, 0.55 kW/cm² at 340 nm with no spray cycle. Failure in this test is determined by the observa-

- 17 -

tion of the physical failure of the sock when it is "scratched" with a blunt glass rod. The longer it takes for this catastrophic failure to occur, the more effective is the stabilizer system. The days to failure are given in Tables 9, 10, 11 and 12 below for each of the stabilization systems.

Table 9:

Stabilizer	Amount	Days to Failure in the WeatherOmeter
HALS 1 Phos I HA A	0.30 % 0.09 % 0.01 %	34
HALS 1 Phos I HA A	0.30 % 0.05 % 0.05 %	38
HALS 1 AO A Phos I HA A	0.30 % 0.05 % 0.05 % 0.05 %	38
HALS 1 AO A Phos I	0.30 % 0.05 % 0.10 %	28

Table 10:

Stabilizer	Amount	Days to Failure in the WeatherOmeter
HALS 2 Phos I HA A	0.30 % 0.09 % 0.01 %	23
HALS 2 Phos I HA A	0.30 % 0.05 % 0.05 %	30

- 18 -

Table 11:

Stabilizer	Amount	Days to Failure in the WeatherOmeter
HALS 3 Phos I HA A	0.30 % 0.09 % 0.01 %	38
HALS 3 Phos I HA A	0.30 % 0.05 % 0.05 %	37

Table 12:

Stabilizer	Amount	Days to Failure in the WeatherOmeter
HALS 2 Phos II HA A	0.05 % 0.05 % 0.05 %	9

Example 4: Long Term Heat Stability of Polypropylene Fiber.

In the long term heat aging at 120°C, other knitted socks of the stabilized polypropylene fiber are exposed in a forced draft oven equipped with a rotating carousel. Again, failure is determined as described above. The longer it takes for such catastrophic failure to occur, the more efficacious is the stabilizer system. The test data are given in Tables 13, 14 and 15 below.

Table 13:

Stabilizer	Amount	Days to Failure at 120°C
HALS 1 Phos I HA A	0.30 % 0.09 % 0.01 %	65
HALS 1 Phos I HA A	0.30 % 0.05 % 0.05 %	61

Table 14:

Stabilizer	Amount	Days to Failure at 120°C
HALS 2 Phos I HA A	0.30 % 0.09 % 0.01 %	40
HALS 2 Phos I HA A	0.30 % 0.05 % 0.05 %	72

Table 15:

Stabilizer	Amount	Days to Failure at 120°C
HALS 3 Phos I HA A	0.30 % 0.09 % 0.01 %	68
HALS 3 Phos I HA A	0.30 % 0.05 % 0.05 %	75

Examples 5-6 show that, in regards to gas fade resistance, the instant stabilization mixture is far superior as measured by Delta E values where low numbers indicate less color. The numerical differences shown are significant, and the samples can be easily differentiated visually.

Example 5: Gas Fade Resistance or Color Stability of Polypropylene Fiber.

Other knitted socks of the stabilized polypropylene fiber are exposed to oxides of nitrogen in an Exposure Chamber using the AATCC Test Method 23-1988, "Colorfastness to Burnt Gas Fumes" for 3 and 7 "cycles". Test specimens are removed from the chamber and assessed for change in color (Delta E color scale) on an Applied Color Systems Model CS-5 colorimeter (D65 illuminant, 2° observer). Low Delta E values indicate less color and better stabilization. The test data are given in Tables 16, 17, 18, 19, 20, 21 and 22 below.

Table 16:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 1 Phos I HA A	0.30 % 0.09 % 0.01 %	2.4	2.8
HALS 1 Phos I HA A	0.30 % 0.05 % 0.05 %	2.3	2.9
HALS 1 AO A Phos I HA A	0.30 % 0.05 % 0.09 % 0.01 %	5.7	6.7
HALS 1 AO A Phos I HA A	0.30 % 0.05 % 0.05 % 0.05 %	4.3	6.1

Table 17:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 1 Phos I HA A	0.05 % 0.09 % 0.01 %	1.9	1.5
HALS 1 Phos I HA A	0.05 % 0.05 % 0.05 %	1.8	1.9
HALS 1 AO A Phos I HA A	0.05 % 0.05 % 0.09 % 0.01 %	3.8	5.2
HALS 1 AO A Phos I HA A	0.05 % 0.05 % 0.05 % 0.05 %	3.2	5.0

Table 18:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 2 Phos I HA A	0.30 % 0.09 % 0.01 %	1.6	1.5
HALS 2 Phos I HA A	0.30 % 0.05 % 0.05 %	1.5	1.9
HALS 2 AO A Phos I HA A	0.30 % 0.05 % 0.09 % 0.01 %	3.9	5.3
HALS 2 AO A Phos I HA A	0.30 % 0.05 % 0.05 % 0.05 %	1.9	3.7

Table 19:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 2 Phos I HA A	0.05 % 0.09 % 0.01 %	1.6	1.5
HALS 2 Phos I HA A	0.05 % 0.05 % 0.05 %	1.0	1.3
HALS 2 AO A Phos I HA A	0.05 % 0.05 % 0.09 % 0.01 %	3.8	4.9
HALS 2 AO A Phos I HA A	0.05 % 0.05 % 0.05 % 0.05 %	2.0	3.9

Table 20:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 3 Phos I HA A	0.30 % 0.09 % 0.01 %	2.4	2.3
HALS 3 Phos I HA A	0.30 % 0.05 % 0.05 %	1.7	1.9
HALS 3 AO A Phos I HA A	0.30 % 0.05 % 0.09 % 0.01 %	4.8	6.7
HALS 3 AO A Phos I HA A	0.30 % 0.05 % 0.05 % 0.05 %	3.1	5.3

Table 21:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 3 Phos I HA A	0.05 % 0.09 % 0.01 %	1.9	1.6
HALS 3 Phos I HA A	0.05 % 0.05 % 0.05 %	1.2	1.3
HALS 3 AO A Phos I HA A	0.05 % 0.05 % 0.09 % 0.01 %	4.0	5.3
HALS 3 AO A Phos I HA A	0.05 % 0.05 % 0.05 % 0.05 %	2.3	4.6

Table 22:

Stabilizer	Amount	Delta E Color after Cycle	
		3	7
HALS 2 Phos II HA A	0.05 % 0.05 % 0.05 %	1.5	1.8
HALS 2 AO A Phos II HA A	0.05 % 0.05 % 0.05 % 0.05 %	1.9	3.1

Example 6: Gas Fade Resistance or Color Stability of Polypropylene Fiber

Other knitted socks of the stabilized polypropylene fiber are exposed to oxides of nitrogen in an Exposure Chamber using the AATCC Test Method 23-1988, "Colorfastness to Burnt Gas Fumes" for 3 "cycles". Test specimens are removed from the chamber and assessed for change in color (Delta E color scale) on an Applied Color Systems Model CS-5 colorimeter (D65 illuminant, 2° observer). The test data are given in Tables 23, 24 and 25 below. Low Delta E values indicate less color and better stabilization.

Table 23:

Stabilizer	Amount	Delta E Color after Cycle 3
HALS 1 Phos I AO A	0.15 % 0.08 % 0.04 %	6.9
HALS 1 Phos I HA A	0.15 % 0.08 % 0.04 %	2.4
HALS 4 Phos I AO A	0.30 % 0.10 % 0.05 %	2.7
HALS 4 Phos I HA A	0.30 % 0.05 % 0.05 %	1.2
HALS 5 Phos I AO A	0.30 % 0.10 % 0.05 %	3.2
HALS 5 Phos I HA A	0.30 % 0.05 % 0.05 %	1.0
HALS 6 Phos I AO A	0.30 % 0.10 % 0.05 %	2.1
HALS 6 Phos I HA A	0.30 % 0.05 % 0.05 %	1.0
HALS 7 Phos I AO A	0.30 % 0.10 % 0.05 %	2.2
HALS 7 Phos I HA A	0.30 % 0.05 % 0.05 %	1.0

Table 24:

Stabilizer	Amount	Delta E Color after Cycle 3
HALS 1 Phos III AO A	0.15 % 0.08 % 0.04 %	5.6
HALS 1 Phos III HA A	0.15 % 0.08 % 0.04 %	3.8

Table 25:

Stabilizer	Amount	Delta E Color after Cycle 3
HALS 1 Phos IV AO A	0.15 % 0.08 % 0.04 %	4.8
HALS 1 Phos IV HA A	0.15 % 0.08 % 0.04 %	2.3

Inspection of the data given above shows that the instant formulations containing other selected hindered amines, other phosphites and hydroxylamines provide excellent gas fade resistance and color stability to polypropylene far superior to the stabilizer systems containing a phenolic antioxidant.

Example 7: Gas Fade Resistance or Color Stability of Polypropylene Fiber

Following the procedure of Example 6, the gas fade resistance or color stability of polypropylene fiber is measured when said fiber is protected by a binary system of stabilizers comprising a hindered amine and a hydroxylamine without the presence of any phosphite compared to fiber with additionally contains a phenolic antioxidant. The test data are given in Tables 26, 27 and 28 below. Low Delta E values indicate less color and better stabilization.

Table 26:

Stabilizer	Amount	Delta E Color after Cycle 3
HALS 1 Phos I AO A	0.05 % 0.10 % 0.05 %	4.7
HALS 1 HA A	0.05 % 0.10 %	1.0
HALS 1 HA A	0.05 % 0.05 %	1.2

Table 27:

Stabilizer	Amount	Delta E Color after Cycle 3
HALS 2 Phos I AO A	0.05 % 0.10 % 0.05 %	4.1
HALS 2 HA A	0.05 % 0.10 %	0.9
HALS 2 HA A	0.05 % 0.05 %	0.9

Table 28:

Stabilizer	Amount	Delta E Color after Cycle 3
HALS 3 Phos I AO A	0.05 % 0.10 % 0.05 %	4.4
HALS 3 HA A	0.05 % 0.10 %	1.0
HALS 3 HA A	0.05 % 0.05 %	0.9

Inspection of the data given above shows that the instant binary formulations containing

selected hindered amines and hydroxylamines provide excellent gas fade resistance and color stability to polypropylene far superior to the stabilizer systems containing a phenolic antioxidant.

Example 8: Process Stabilization of Polypropylene Fiber

Melt flow differences resulting from insufficient processing stability are quite evident when the polypropylene is spun under severe processing conditions. This is particularly evident when polypropylene is spun at 302°C. The lower the melt flow rates are the more effective is the process stabilization efficacy of the stabilizer system (see also example 1). The melt flow values of polypropylene spun at that temperature are shown in the Tables 29, 30 and 31 below.

Table 29:

Stabilizer	Amount	Melt Flow Rate Fiber Spun at 302°C
HALS 1	0.05 %	65
HALS 1 Phos I	0.05 % 0.10 %	34
HALS 1 Phos I AO A	0.05 % 0.10 % 0.05 %	16
HALS 1 Phos I HA A	0.05 % 0.05 % 0.05 %	18
HALS 1 HA A	0.05 % 0.05 %	18

Table 30:

Stabilizer	Amount	Melt Flow Rate Fiber Spun at 302°C
HALS 2	0.05 %	56
HALS 2 Phos I	0.05 % 0.10 %	24
HALS 2 Phos I AO A	0.05 % 0.10 % 0.05 %	15
HALS 2 Phos I HA A	0.05 % 0.05 % 0.05 %	19
HALS 2 HA A	0.05 % 0.05 %	18

Table 31:

Stabilizer	Amount	Melt Flow Rate Fiber Spun at 302°C
HALS 3	0.05 %	28
HALS 3 Phos I	0.05 % 0.10 %	31
HALS 3 Phos I AO A	0.05 % 0.10 % 0.05 %	16
HALS 3 Phos I HA A	0.05 % 0.05 % 0.05 %	17
HALS 3 HA A	0.05 % 0.05 %	17

The data in Tables 29, 30 and 31 clearly show that in a conventional stabilizer system a combination of phenolic antioxidant, hindered amine and phosphite provide good processing stability. The removal of the phenolic antioxidant results in a significant loss in process stabilization. However, the substitution of a hydroxylamine in place of the phenolic antioxidant yields process stabilization fully comparable to that provided by the

- 29 -

phenolic antioxidant-phosphite system both in the presence or absence of the phosphite component. Thus the binary stabilizer system of hindered amine plus hydroxylamine provides excellent thermal process stabilization to the polypropylene fiber.

- 30 -

WHAT IS CLAIMED IS:

1. A stabilized polypropylene fiber, free or essentially free of any phenolic antioxidant, and having enhanced light stability, enhanced long term heat stability and enhanced gas fade resistance, which fiber is stabilized by a mixture of

a) a hindered amine selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;
 the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;
 N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;
 the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;
 poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;
 bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethylmalonate;
 1,3,5-tris(N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-s-triazine);
 the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-cyclohexylamino-s-triazine; and
 poly{N-[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,4,7-triazanonane}- ω -N''-[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]amine;

b) a phosphite selected from the group consisting of

tris(2,4-di-tert-butylphenyl) phosphite;
 3,9-di(2,4-di-tert-butylphenyl)-2,4,8,10-tetraoxa-3,9-diphospha[5.5]undecane;
 2,2',2''-nitrido-tris[ethyl (3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite];
 ethyl bis(2,4-di-tert-butyl-6-methylphenyl) phosphite; and
 tetrakis(2,4-di-tert-butylphenyl)-4,4'-bis(diphenylene)phosphonite; and

c) a hydroxylamine selected from the group consisting of

- 31 -

N,N-diocetadecylhydroxylamine;

N,N-dialkylhydroxylamine of the formula T_1T_2NOH where T_1 and T_2 are the alkyl mixture found in hydrogenated tallow amine; and

the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901;

wherein the weight ratio of components (a):(b):(c) is from 1:1:1 to 100:2:1.

2. A stabilized fiber according to claim 1 wherein component (a) is selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;

the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;

N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;

poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;

bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethylmalonate; and

1,3,5-tris[N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-s-triazine.

3. A stabilized fiber according to claim 1 wherein component (b) is selected from the group consisting of

tris(2,4-di-tert-butylphenyl) phosphite;

3,9-di(2,4-di-tert-butylphenyl)-2,4,8,10-tetraoxa-3,9-diphospha[5.5]undecane;

2,2',2''-nitrido-tris[ethyl (3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite];

and

ethyl bis(2,4-di-tert-butyl-6-methylphenyl) phosphite.

4. A stabilized fiber according to claim 1 wherein component (c) is the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)-amine by the process of US-A-5 013 510 or US-A-4 898 901.

- 32 -

5. A stabilized fiber according to claim 1 wherein the weight ratio of components (a):(b):(c) is from 10:1:1 to 10:2:1.
6. A stabilized fiber according to claim 1 wherein the amount of the mixture of stabilizers is from 0.05 to 5 % by weight based on the weight of the fiber.
7. A method for enhancing gas fade resistance and reducing color formation in stabilized polypropylene fiber, without the loss of any other stabilization property, by incorporating therein a mixture of stabilizers according to claim 1.
8. A method for enhancing the resistance to degradation of polypropylene fiber, due to exposure to UV radiation over that which can be achieved by the use of conventional stabilizers alone, by incorporating therein a mixture of stabilizers according to claim 1.
9. A method for enhancing the thermal stability of polypropylene fiber, over that which can be achieved by the use of conventional stabilizers alone, by incorporating therein a mixture of stabilizers according to claim 1.
10. A stabilized polypropylene fiber, free or essentially free of any phenolic antioxidant, and having enhanced light stability, enhanced long term heat stability and enhanced gas fade resistance, which fiber is stabilized by a mixture of

I) a hindered amine selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;

the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;

N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane;

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;

poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propyl]siloxane;

bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxydimethylmalonate;

1,3,5-tris{N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-

- 33 -

s-triazine; and
the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethyl-piperidine) and 2,4-dichloro-6-cyclohexylamino-s-triazine; and

II) a hydroxylamine selected from the group consisting of

N,N-dioctadecylhydroxylamine;
N,N-dialkylhydroxylamine of the formula T_1T_2NOH where T_1 and T_2 are the alkyl mixture found in hydrogenated tallow amine; and
the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine by the process of US-A-5 013 510 or US-A-4 898 901;

wherein the weight ratio of components (I):(II) is from 100:1 to 1:2.

11. A stabilized fiber according to claim 10 wherein component (I) is selected from the group consisting of

the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethyl-piperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;
the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid; and
N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane.

12. A stabilized fiber according to claim 10 wherein component (II) is the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)-amine by the process of US-A-5 013 510 or US-A-4 898 901.

13. A stabilized fiber according to claim 10 wherein the weight ratio of components (I):(II) is from 10:1 to 1:1.

14. A stabilized fiber according to claim 10 wherein the amount of the mixture of stabilizers is from 0.05 to 5 % by weight based on the weight of the fiber.

15. A method for enhancing gas fade resistance and reducing color formation in stabilized polypropylene fiber, without the loss of any other stabilization property, by incorporating

- 34 -

therein a mixture of stabilizers according to claim 10.

16. A method for enhancing the resistance to degradation of polypropylene fiber, due to exposure to UV radiation over that which can be achieved by the use of conventional stabilizers alone, by incorporating therein a mixture of stabilizers according to claim 10.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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C08K5/524

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 D01F C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 323 409 (CIBA-GEIGY AG) 5 July 1989 cited in the application see claims; examples 22,25	1-16
Y	EP,A,0 276 923 (TONEN SEKIYUKAGAKU K. K.) 3 August 1988 see page 2, line 12 - line 45; claims; example 13	1-16
A	EP,A,0 138 767 (CIBA-GEIGY AG) 24 April 1985 cited in the application see claims; examples 5,6,11	1,10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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